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(54) Title: DECOMPOSITION OF FLUORINE CONTAINING COMPOUNDS

(57) Abstract: A process for the decomposition and removal of one or more fluorine containing compounds from a first gaseous mixture comprising the one or more fluorine containing compounds and water vapour, which process comprises the stages of: (i) contacting the first gaseous mixture with a catalyst comprising an aluminium based material to produce a second gaseous mixture comprising hydrogen fluoride and carbon oxides; and (ii) removing the hydrogen fluoride from the second gaseous mixture to produce a third gaseous mixture, which is substantially free of hydrogen fluoride.



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Decomposition of Fluorine Containing Compounds

This invention relates to a catalytic abatement process for decomposing one or more fluorine containing compounds in an aqueous gaseous mixture.

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Fluorine containing compounds, such as hydrofluorocarbons and perfluorocarbons, are generated as by-products in a number of different industrial processes.

10 For example, in the semiconductor industry perfluorocarbons are used as cleaning and etching agents in the wafer fabrication process. Generally, the perfluorocarbons are fragmented to produce fluorine species that etch the wafer surface, creating fluorine containing by-products such as SiF_4 . However, only about 20 to 30% of the perfluorocarbon gas is actually used
15 in the process. The perfluorocarbons that are not used in the process are often emitted into the atmosphere.

The aluminium smelting and processing industry also generates vast quantities of perfluorocarbons. These processes produce significant
20 amounts of perfluorocarbons, which are emitted into the atmosphere. The species predominantly formed are tetrafluoromethane and perfluoroethane.

Perfluorocarbons have been shown to contribute to global warming. Emissions of these gases into the atmosphere should, therefore, be avoided.
25 One way of achieving this is to destroy the perfluorocarbons so as to produce products that are more environmentally friendly.

Several methods for the recovery and abatement of perfluorocarbons are known. These methods generally comprise combustion, catalytic and
30 plasma based technologies. Recovery techniques generally comprise

solvation, membrane and cryogenic distillation processes. Processes for the recovery of perfluorocarbons are, however, often not economically viable as the exhaust gas streams are typically dilute and typically only comprise from 2 to 3% perfluorocarbons.

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US-A-6077482 describes a process for decomposing organohalogen compounds such as chlorofluorocarbons. A catalyst comprising titania and tungsten oxide is contacted with the organohalogen compounds at a temperature of from 200 to 500°C.

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JP-A-10192653 describes a process in which a gas stream containing at least one compound containing a fluorine atom and at least two carbon atoms is contacted with a catalyst containing alumina, titania, silica and zirconia in the presence of steam at a temperature of from 204 to 427°C.

15 The catalyst activity was found to decrease over time due to the formation of aluminium fluoride.

In both these examples a wet alkaline scrubber or an alkaline filter is used to remove hydrogen fluoride by-products at the end of the process.

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There are, however, a number of disadvantages associated with using wet scrubbing systems. For example, corrosion of ducting and instruments associated with the process occurs readily. Ducts also become blocked because silica forms within them. The handling of aqueous hydrogen fluoride also has a number of problems associated with it, such as safety, neutralisation and disposal. It is also necessary to ensure that heavy metals such as copper and tungsten are removed from the liquors of the aqueous scrubbing systems as they are also harmful to the environment.

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The use of alumina as a catalyst to hydrolyse perfluorocarbons has also been investigated. Alumina was found to be ineffective as a catalyst because the hydrolysis reaction is inhibited due to the conversion of alumina to aluminium trifluoride (see Catalytic control of emissions during semiconductor manufacture, Brown R., Rossin J.A., SIA Semicon west 2000). Aluminium trifluoride is formed by reaction of alumina with hydrogen fluoride produced in the hydrolysis reaction.

Thus, there is a need for an improved process for the decomposition of perfluorocarbons in gaseous product streams which is simple, effective and industrially applicable.

The present invention provides a catalytic abatement process for decomposing one or more fluorine containing compounds in a gaseous mixture containing water vapour.

In the process of the present invention, firstly fluorine containing species in the gaseous mixture are hydrolysed and secondly hydrogen fluoride and other fluorine containing species are removed.

The process of the present invention is a two stage hydro-thermal treatment process for a stream comprising one or more fluorine containing compounds. In the first stage the fluorine containing compound(s) are hydrolysed using a catalyst comprising an aluminium based material, thus producing hydrogen fluoride and carbon oxides. In the second stage hydrogen fluoride is removed from the product of the first stage. This second stage may be performed using a solid comprising an aluminium based material, such as an alumina, hydrated aluminium oxide or aluminium hydroxide containing material, as a hydrogen fluoride absorbent which may be referred to or termed the second stage catalyst.

The two stage process provides a high efficiency of decomposition of the fluorine containing compounds, where destruction efficiencies of greater than 99% may be achieved. Levels of hydrogen fluoride emission are negligible. Typically, the absorption efficiency is greater than 99%. Thus,
5 the process of the invention removes the need for aqueous scrubbing post treatments.

In a preferred embodiment of the invention, the two stage process of the invention is repeated. In other words, in this embodiment the process
10 comprises a hydrolysis step then an absorption step which are followed by a further hydrolysis step and absorption step. The two stage process may be repeated as many times as necessary.

In another embodiment of the invention, at least part of the gaseous product
15 of the second stage (ii) of the process is recycled to the first stage (i).

In another embodiment, the perfluorocarbon concentration in the feed stream can be concentrated prior to being fed to the two stage process. This allows the volume of gas passing through the process to be reduced, providing smaller process reactors to be used at a higher energy efficiency.
20 A range of technologies may be used to concentrate the perfluorocarbon concentration in the feed stream including pressure swing or temperature swing adsorption/desorption, membranes, condensation and the solvent extraction of the perfluorocarbons from the gas stream to be treated. In the
25 aluminium production industry, the use of zeolite adsorbents to trap and concentrate very dilute CF_4 from large gaseous vent streams may be particularly advantageous, when used with the two stage process of the present invention.

The process of the present invention can be conducted at lower temperatures than those used in alternative catalytic and combustion processes for perfluorocarbon abatement. The use of lower temperatures helps to prevent the formation of NO_x by-products.

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According to the present invention there is provided a process for the decomposition and removal of one or more fluorine containing compounds from a first gaseous mixture comprising the one or more fluorine containing compounds and water vapour, which process comprises the stages of (i) contacting the first gaseous mixture with a catalyst comprising an aluminium based material to produce a second gaseous mixture comprising hydrogen fluoride and carbon oxides; and (ii) removing the hydrogen fluoride from the second gaseous mixture to produce a third gaseous mixture, which is substantially free of hydrogen fluoride.

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Stage (i) of the process is a hydrolysis reaction. It is, therefore, essential that the first gaseous mixture comprises water vapour. Typically, the number of hydrogen atoms provided by the water is at least equal to the total number of fluorine atoms provided by the fluorine containing compounds, i.e. at least a stoichiometric level of water to convert all fluorine containing compounds to oxides and hydrogen fluoride.

20

Preferably, the water level fed to the hydrolyser in stage (i) of the process should be sufficient to fully hydrolyse 1 to 100 times the quantity of fluorine containing compounds in the first gaseous mixture. More preferably, the level of excess water should be 1.5 to 40 times, most preferably 2 to 10 times, more than the stoichiometric requirement for full hydrolysis of the fluorine containing compounds in the first gaseous mixture.

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The fluorine containing compounds which may be decomposed using the process of the present invention include hydrofluorocarbons and perfluorocarbons, which may be saturated or unsaturated. The fluorine containing compounds may also contain other heteroatoms such as chlorine.

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By the term "hydrofluorocarbon" we mean compounds that contain only carbon, hydrogen and fluorine atoms in their structure. By the term "perfluorocarbons" we mean compounds that contain only carbon and fluorine in their structure.

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Preferably, the fluorine containing compounds such as hydrofluorocarbons and perfluorocarbons comprise from one to twelve carbon atoms, more preferably from one to six carbon atoms and still more preferably from one to four carbon atoms. Typically, the fluorine containing compounds are

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straight or branched chain or cyclic organic compounds.

Particularly preferred hydrofluorocarbons and perfluorocarbons include tetrafluoromethane, trifluoromethane, perfluoroethane, perfluoropropane, octafluorobutane (both isomers), pentafluoroethane (R125),

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difluoromethane (R32) and tetrafluoroethane (R134a). Still more preferably, the fluorine containing compound is tetrafluoromethane or perfluoroethane.

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Suitable catalysts comprising an aluminium based material for use in the first stage of the process of the invention include aluminium oxide (alumina), hydrated aluminium oxide, aluminium hydroxide, aluminium oxyfluoride and aluminium fluoride.

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The operating catalyst typically has a surface area of $5\text{ m}^2/\text{g}$ or greater, preferably $10\text{ m}^2/\text{g}$ or greater and more preferably $20\text{ m}^2/\text{g}$ or greater. It is

most preferred that the catalyst has a surface area of $40 \text{ m}^2/\text{g}$ or greater. As the hydrolysis conditions cause a progressive loss of surface area, the preferred catalysts comprising an aluminium based material have an initial surface area of $5 \text{ m}^2/\text{g}$ or greater, more preferably $50 \text{ m}^2/\text{g}$ or greater. The preferred catalysts comprising an aluminium based material also have a high thermal stability in the high temperature hydrolysis conditions and in the presence of water and hydrogen fluoride gases.

Suitable absorbents comprising an aluminium based material for use in the second stage of the process of the invention include aluminium oxide (alumina), hydrated aluminium oxide, aluminium hydroxide and aluminium oxyfluoride. Preferably the absorbent used in the second stage has a high surface area. The use of absorbents having a surface area of at least $50 \text{ m}^2/\text{g}$ is preferred. For example, alumina having a surface area of $200 \text{ m}^2/\text{g}$ or greater can be used.

In a preferred embodiment of the process, the same aluminium based material may be used in the first stage and the second stage. In this case, the same aluminium based material may be used in the second stage before it is used in the first stage. Thus, it is not essential for the aluminium based material used in the first stage to be "fresh" ie, it may be contaminated to some extent with, for example, hydrogen fluoride, or be partly converted to aluminium fluoride.

Preferably, the aluminium based materials used possess sufficient thermal stability to retain a surface area of $20 \text{ m}^2/\text{g}$ or greater in the stage (i) hydrolysis reactor and thus provide sustained high levels of fluorocarbon destruction.

The aluminium based material used in either stage (i) or stage (ii) may be subjected to pre-treatment prior to use. For example, the aluminium based material may be pre-treated by being subjected to thermal or hydrothermal treatments. Hydrothermal treatment is especially favourable for aluminium based materials with high fluoride contents, as high temperature steam treatments increase the surface oxide contents and the associated fluorochemical hydrolysis activity of the aluminium based material.

Steam increases the oxide level on the aluminium based material and hence increases the activity of the material as a catalyst. For example, steam passed over a catalyst comprising an aluminium based material introduces oxides into the structure. Thus, steam treatment can be considered to be an activation step that increases the performance of the catalyst. Steam can also be used to regenerate a previously used catalyst. Additionally, steam can be used to recover a heavily fluorinated catalyst and to recover the catalyst from an upset condition.

During steam treatment water vapour is passed through the catalyst bed. This is typically carried out at a temperature of greater than 500°C, preferably from 600 to 800°C. The steam treatment typically takes from 1 to 60 minutes, preferably about 10 minutes, at 700 to 750°C.

Stage (i) of the process of the invention is typically conducted at a temperature of 450°C or more, and preferably at a temperature of from 500 to 1000°C, more preferably at a temperature of from 650 to 800°C, for example at about 700 to 750°C.

Stage (i) of the process of the invention can be carried out at atmospheric, subatmospheric or superatmospheric pressure. Preferably, stage (i) is

carried out at atmospheric pressure or at a pressure a little above or below atmospheric pressure.

Stage (i) of the process produces hydrogen fluoride and carbon oxides.

- 5 Operation of the unit at sub-atmospheric pressure reduces the risk of gaseous emissions from the reaction zone, which contains toxic hydrogen fluoride and carbon monoxide gases.

- 10 Typically, stage (i) of the process of the present invention provides a 99% conversion of the perfluorocarbons and hydrofluorocarbons.

- 15 High proportions of carbon monoxide may be formed in the hydrolysis of hydrofluorocarbons and higher molecular weight perfluorocarbons. Air may be added to the first gaseous mixture in order to reduce the level of carbon monoxide formed. The air oxidises the carbon monoxide to carbon dioxide, which can be released into the atmosphere without further treatment.

- 20 The efficacy of stage (i) of the process may be increased by the addition of additives to the catalyst comprising an aluminium based material. Suitable additives include the metals of Groups 4 to 14 of the periodic table of elements and compounds comprising one or more metals from these groups. These improve alumina hydrothermal stability and thus surface area retention in the hydrolysis reactor of stage (i). Zinc oxide is an example of a useful alumina stabiliser for the process of the invention. Redox metals
25 within the above Groups also increase the carbon monoxide oxidation rates in the process. Iron or compounds of iron are preferred. For example, oxides, hydroxides or hydrated oxides of iron may be mixed with the catalyst comprising an aluminium based material.

The reference to Groups 4 to 14 of the periodic table of the elements refers to the new IUPAC version of the periodic table of elements.

For example, zinc or a zinc compound such as zinc oxide can be added to the catalyst in order to improve hydrolysis. For example, the use of zinc or a zinc containing compound may increase surface area stability and thus increase the length of time for which the catalyst is active. Iron or an iron containing compound can be added to increase carbon monoxide oxidation rates. Suitable iron containing compounds include iron oxides, such as Fe_2O_3 .

A particularly preferred catalyst comprises zinc and Fe_2O_3 on an aluminium oxyfluoride support. Another preferred catalyst comprises zinc on an alumina support.

Another particularly preferred catalyst is an aluminium based catalyst comprising an aluminium oxide, hydrated aluminium oxide, aluminium hydroxide, aluminium oxyfluoride or aluminium fluoride, with a surface area of $50 \text{ m}^2/\text{g}$ or greater and a pore volume of 0.3 cc/g or greater. The surface area of the catalyst is located in the pores, which have a diameter of 40 \AA or greater, preferably 50 \AA or greater. Preferred alumina based catalysts have a combined alkali and alkaline earth metal content of less than 1% w/w, more preferably less than 0.5% w/w.

Water vapour can be injected into the first gaseous mixture in order to promote hydrolysis.

In stage (ii) of the process of the invention, the hydrogen fluoride can be removed from the second gaseous mixture by any suitable method. For example hydrogen fluoride can be removed using methods well known in

the art such as water scrubbing, aqueous alkali scrubbing, reaction with alkaline metal earth metal oxides and absorption into an amine hydrohalide, a glycol or sulphuric acid.

- 5 In a preferred aspect of the present invention, hydrogen fluoride may be removed from the second gaseous mixture by contacting it with an absorbent comprising an aluminium based material, such as aluminium oxide, hydrated aluminium oxide, aluminium hydroxide or aluminium oxyfluoride. Alumina based materials with low silica contents are
10 preferred, as such materials limit the amount of volatile fluorine containing compounds of silicon entering the process vent stream.

The aluminium based material used in the second stage may be subjected to pre-treatment prior to use. For example, steam treatment, as described
15 above, may be used.

Preferably, the second gaseous mixture is contacted with the absorbent comprising an aluminium based material at a temperature of 500°C or less, more preferably 400°C or less and most preferably at a temperature of from
20 275 to 375°C, for example, 350°C. It is preferred that stage (ii) of the process is conducted at a temperature below the temperature at which stage (i) is conducted.

The second stage of the process of the invention may be carried out at
25 atmospheric, subatmospheric or superatmospheric pressure. Preferably, the second stage is carried out at atmospheric pressure or at a pressure a little above or below atmospheric pressure. Preferably, the second stage of the process of the invention is carried out at the same pressure or a similar pressure to the first stage of the process.

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The same aluminium based material may be used in both stages (i) and (ii) of the process of the invention. It is preferred that the aluminium based material used in stage (ii) is also used as the aluminium based material for stage (i). This can be achieved by using a moving bed to move the aluminium based material from the reaction zone for stage (ii) to the reaction zone for stage (i). In this example, the bed moves in a direction counter-current to the gas flow.

In an alternative embodiment, in stage (ii) of the process the hydrogen fluoride may be removed from the second mixture by absorbing the hydrogen fluoride using a conventional alkali or water scrubber.

The reaction residence time for each stage of the process of the invention is preferably up to about 40 seconds, preferably from 0.1 to 10 seconds, and more preferably from 0.2 to 5 seconds under reaction conditions.

The process of the invention may comprise a third stage (iii) in which materials other than fluorine containing organic entities can be removed from the first gaseous mixture in a pre-treatment step before the first gaseous mixture is subjected to stage (i). For example, other fluorine containing compounds such as non-organic fluorine containing compounds, for example SiF_4 and WF_6 can be removed. These materials can be removed using methods that are conventional in the art such as by the use of water scrubbers.

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Alternatively, inorganic fluorine containing compounds can be removed from a gaseous mixture comprising these compounds and one or more organic fluorine containing compounds by passing the gaseous mixture over an aluminium based material. Suitable aluminium based materials include those described above, for example, aluminium oxide (alumina), hydrated

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aluminium oxide, aluminium hydroxide, aluminium oxyfluoride and aluminium fluoride. These aluminium based materials may contain additives as described above.

- 5 The inorganic fluorine containing compounds may be removed from the first gaseous mixture by hydrolysis to an oxide or oxyfluoride, where the inorganic compound is deposited on a solid comprising aluminium oxide, hydrated aluminium oxide, aluminium hydroxide, aluminium oxyfluoride or aluminium fluoride. The inorganic fluorine containing compound may be
- 10 deposited on the aluminium based material used in stage (i). The inorganic fluorine containing compound is typically deposited on the aluminium based material at a temperature below 800°C, for example from 0 to 500°C, and a lower temperature than that at which stage (i) is conducted.
- 15 The stage for removing the inorganic fluorine containing compounds is preferably used as a pre-treatment step in combination with the two stage process of the present invention. Thus, the present invention also provides a three stage process comprising pre-treatment of the first gaseous mixture to remove inorganic fluorine containing compounds followed by the two stage
- 20 process described above.

Preferably, the stage for removing inorganic fluorine containing compounds is conducted at a temperature of from 100 to 800°C, more preferably from 200 to 500°C. When this process is carried out in combination with the two

25 stage process of the invention the temperature at which this process is carried out is typically lower than that used in the first stage (i) of the two stage process.

The reaction residence time of stage (iii) is preferably from 0.1 to 30

30 seconds.

The stage for removing inorganic fluorine containing compounds is typically carried out at atmospheric, subatmospheric or superatmospheric pressure. Preferably atmospheric pressure or a pressure a little above or below atmospheric pressure is used. If this stage is carried out in combination with the two stage process described above this stage (iii) is preferably carried out at the same or similar pressure as used in the first stage of the two stage process, more preferably at the same or similar pressure as used in both stages of the two stage process.

When the stage (iii) for removing inorganic fluorine containing compounds is carried out in combination with the two stage process described above the aluminium based material used in stage (iii) is preferably the same as that used in one or both of the other two stages. Most preferably, the same aluminium based material is used in all three stages. In this case, spent aluminium based material from stages (i) and (ii) can be used in the process for removing non-organic fluorine containing compounds.

It is preferred that at least a proportion of the gas vented from stage (ii) of the process is recycled to the reaction zone for stage (i) and/or stage (iii).

The apparatus that may be used to carry out the processes of the present invention may employ a moving bed of aluminium based material, which moves counter current to the gas flow. Preferably the moving bed will pass through the reaction zones for both stages of the two stage process. If the stage for removing inorganic fluorine containing compounds is also used, the moving bed will preferably also pass through the reaction zone for this stage. Thus, in a preferred embodiment the aluminium based material initially passes through the reaction zone for the second stage (ii) of the process and then through the reaction zone for the first stage (i) of the

process and then, optionally, through the reaction zone for the stage (iii) for removing inorganic fluorine containing compounds.

It will be appreciated that when a three stage process is used, stages (i) and (ii) may be repeated as described above. Also, when a three stage process is used the gaseous product from stage (ii) may be recycled either into the reaction zone for stage (i) or into the reaction zone for stage (iii).

An example of a suitable apparatus in which the two stage process of the present invention may be conducted will now be described, by way of non-limiting example, with reference to Figure 1.

Figure 1 shows an apparatus suitable for use in the process of the present invention. Using the apparatus of Figure 1 the same aluminium based material is used for both stages (i) and (ii) of the process.

The apparatus (10) comprises first and second reaction zones, (12) and (14). A first gaseous mixture comprising one or more fluorine containing compounds and water vapour is fed into the first reaction zone (12) at inlet (16). This mixture passes through the first reaction zone (12) and then through the second reaction zone (14).

Whilst the first gaseous mixture is fed into the apparatus, a catalyst comprising an aluminium based material is fed into the second reaction zone (14) at inlet (18). The direction in which the aluminium based material flows is opposite to that in which the first gaseous mixture flows. The aluminium based material passes through the second reaction zone (14) and then the first reaction zone (12) and contacts the first gaseous mixture.

As the first gaseous mixture passes through the two reaction zones, it contacts the aluminium based material so that fluorine containing species are decomposed and removed. In the first reaction zone the hydrofluorocarbons and/or perfluorocarbons are decomposed. In the second
5 reaction zone, the hydrogen fluoride is removed. Gas substantially free of fluorine containing species exits the apparatus (10) at exit (20). The spent aluminium based material exits the apparatus (10) at exit (22).

The spent aluminium based material, from the two stage process or the
10 process for removing non-organic fluorine containing compounds, may either be reprocessed or disposed of. It is especially preferred to recycle the aluminium based material when the catalytic abatement process is used in the aluminium industry where the recycled materials can be fed into smelters.

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The process is exemplified but not restricted by the following examples.

Example 1 – Stage (i) of the process of the invention

20 A hydrolysis catalyst comprising an aluminium based material was prepared using alumina with a pore volume of greater than 0.3 cc/g and a surface area of greater than 50 m²/g in pores of greater than 50 Å. The alumina was supplied by Engelhard and was coded Al-3996-R. The alumina had a surface area of 200 m²/g and a pore volume of 0.75 cc/g. The alumina was
25 chosen to be low in alkali metal content, having a sodium content of 0.01 %w/w.

The alumina catalyst thus formed was then used as a catalyst for a process corresponding to stage (i) of the process of the present invention.

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The solid extrudate was crushed and sieved to generate alumina particles having a particle size of from 0.5 to 1.5 mm. The alumina particles were packed into an inconel reaction tube with an internal diameter of 8 mm and located in a tube heater to provide a stage (i) reactor. The alumina had a
5 packed bed density of 0.59 g/cc. A stream of nitrogen was saturated in water at 20°C and combined with a stream of carbon tetrafluoride to make a gas mixture containing 5000 parts per million of carbon tetrafluoride by volume. The H₂O:CF₄ feed ratio was estimated to be approximately 20000:5000 by volume, which was double the water requirement for the
10 stoichiometric hydrolysis reaction of CF₄ to CO₂.

The moist nitrogen and CF₄ gas mixture was passed over the alumina catalyst at atmospheric pressure, and the stage (i) reactor was then heated to 700°C. The contact time of the reaction gas mixture under the 700°C
15 reaction conditions was 4.4 seconds. After 12 hours of reaction, the levels of CF₄, CO₂ and HF in the vent stream were measured and the CF₄ hydrolysis efficiency was calculated to be greater than 90%. After the 12 hours of reaction, less than 5% of the HF hydrolysis product was absorbed on the stage (i) alumina catalyst. The catalyst in the high temperature
20 hydrolysis reactor was calculated to have a low HF absorption efficiency with less than 10% of the aluminium oxide content converting to AlF₃.

Example 2 – Stage (ii) of the process of the invention

25 A second inconel reactor was charged with 0.5 to 1.5 mm particles of Engelhard Al-3996-R alumina to provide a stage (ii) reactor. The reactor was heated to 250°C and connected to the vent gas line from the stage (i) reactor of Example 1. The level of HF in the gases vented from the stage (ii) reactor was low, indicating that the HF absorption efficiency was
30 99.4%, when using a contact time of 1.2 seconds. After 15 hours of

operation the HF absorber efficiency decreased sharply and after 20 hours the absorbent failed to absorb additional HF. The alumina in the absorption stage was calculated to have a high HF absorption efficiency with greater than 60% of the aluminium oxide content converting to AlF_3 .

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Example 3 – Stage (ii) of the process of the invention

The spent absorbent was discharged from the stage (ii) reactor and was replaced by an identical fresh alumina charge of Engelhard Al-3996-R alumina. The stage (ii) reactor was heated to 150°C and connected to the vent gas line from the stage (i) reactor operating at 700°C , as described in Example 1. The CF_4 hydrolysis efficiency of the first stage reactor remained high, with above 90% of the CF_4 being converted to CO_2 and HF. The HF absorption efficiency of the stage (ii) alumina charge was found to be 99.4% over the first 10 hours of reaction, when using a contact time of 1.4 seconds. After 13 hours of operation, the stage (ii) alumina bed was exhausted and failed to absorb significant additional levels of the HF produced in stage (i). The aluminium oxide in stage (ii) had been 34% converted to AlF_3 .

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Example 4 – Stages (i) and (ii) of the process of the invention

The reactors used in Example 3 were emptied and the exhausted absorbent from the stage (ii) reactor was placed into the stage (i) hydrolysis reactor. The stage (ii) absorbent charge was replaced, using a repeat charge of fresh Engelhard Al-3996-R alumina. The temperature of the stage (i) reactor was raised to 750°C and the stage (ii) absorber was heated to 250°C , whilst passing a water saturated nitrogen stream containing 2500 ppm by volume of CF_4 . The $\text{H}_2\text{O}:\text{CF}_4$ feed ratio was estimated to be approximately 20000:2500 by volume, which was four times the water requirement for the

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stoichiometric hydrolysis reaction of CF_4 to CO_2 . The contact times employed under reaction conditions were 2.1 seconds in stage (i) and 4.2 seconds in stage (ii), where equal volumes of solid were charged to both stages of the process. After 100 hours of operation, the CF_4 destruction efficiency was maintained at greater than 90%, using the cascaded spent alumina absorbent. The HF absorption efficiency was found to be 99.6%, prior to exhaustion of the HF absorption capacity. The stage (ii) charge of aluminium oxide was found to convert 70% to AlF_3 in this study.

10 Example 5 - Stages (i) and (ii) of the process of the invention

Equal masses of the fresh alumina catalyst detailed in Example 1 were charged to the two stages of the process. The stage (i) reactor was then heated to 750°C and the stage (ii) reactor was heated to 350°C , whilst passing a water saturated nitrogen stream containing 2500 ppm by volume of CF_4 , as described in Example 4. The contact time in the first hydrolysis reaction stage was 2.1 seconds and the contact time in the second stage HF absorber was 3.5 seconds under reaction conditions. The two stage CF_4 destruction process was operated until the second stage alumina absorbent was exhausted and the hydrolysis HF appeared in the vent from the second reaction stage. The two stage reactor system was operated for 92 hours and the CF_4 destruction efficiency was sustained above 99.5%. The HF absorbed by the two stage process was sufficient to convert 66% of the second stage aluminium oxide to AlF_3 .

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Example 6 - Stages (i) and (ii) of the process of the invention

The two reactors used in Example 5 were emptied and the spent absorbent was transferred to the stage (i) hydrolysis reactor. The stage (ii) absorber was recharged with fresh alumina as described in Example 5. The stage (i)

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reactor was then heated to 750°C and the stage (ii) reactor was heated to 400°C, whilst passing a water saturated nitrogen stream containing 2500 ppm by volume of CF₄, as described in Example 4. The contact time in the first hydrolysis reaction stage was 2.1 seconds and the contact time second
5 stage HF absorber was 3.2 seconds under reaction conditions. The two stage reactor system was operated for 50 hours and the CF₄ destruction efficiency was sustained above 99.0%. The HF absorbed by the two stage process was sufficient to convert only 22% of the second stage aluminium oxide to AlF₃.

Claims

1. A process for the decomposition and removal of one or more fluorine containing compounds from a first gaseous mixture comprising the one or
5 more fluorine containing compounds and water vapour, which process comprises the stages of:
 - (i) contacting the first gaseous mixture with a catalyst comprising an aluminium based material to produce a second gaseous mixture comprising hydrogen fluoride and carbon oxides; and
 - 10 (ii) removing the hydrogen fluoride from the second gaseous mixture to produce a third gaseous mixture, which is substantially free of hydrogen fluoride.
2. A process according to claim 1, wherein at least one of the fluorine
15 containing compounds is a hydrofluorocarbon or a perfluorocarbon.
3. A process according to claim 2, wherein the hydrofluorocarbon or perfluorocarbon has a carbon chain length of from one to four.
- 20 4. A process according to claim 2 or 3, wherein the hydrofluorocarbon or perfluorocarbon is tetrafluoromethane, trifluoromethane, perfluoroethane, perfluoropropane, octafluorobutane, pentafluoroethane, difluoromethane or tetrafluoroethane.
- 25 5. A process according to claim 4, wherein the perfluorocarbon is tetrafluoromethane or perfluoroethane.
6. A process according to any one of the preceding claims, wherein in stage (ii) the hydrogen fluoride is removed from the second mixture by

contacting the second gaseous mixture with an absorbent comprising an aluminium based material.

7. A process according to any one of the preceding claims, wherein the catalyst used in stage (i) comprises aluminium oxide, hydrated aluminium oxide, aluminium hydroxide, aluminium oxyfluoride or aluminium fluoride.

8. A process according to claim 6 or 7, wherein the absorbent used in stage (ii) comprises aluminium oxide, hydrated aluminium oxide, aluminium hydroxide or aluminium oxyfluoride.

9. A process according to any one of the claims 6 to 8, wherein the same aluminium based material is used in both stages (i) and (ii).

10. A process according to any one of the preceding claims, wherein stage (i) is conducted at a temperature in the range of from 500 to 1000°C.

11. A process according to any one of the preceding claims, wherein the aluminium based material or at least one of the aluminium based materials comprises at least one metal or compound of a metal of Groups 4 to 14 of the periodic table.

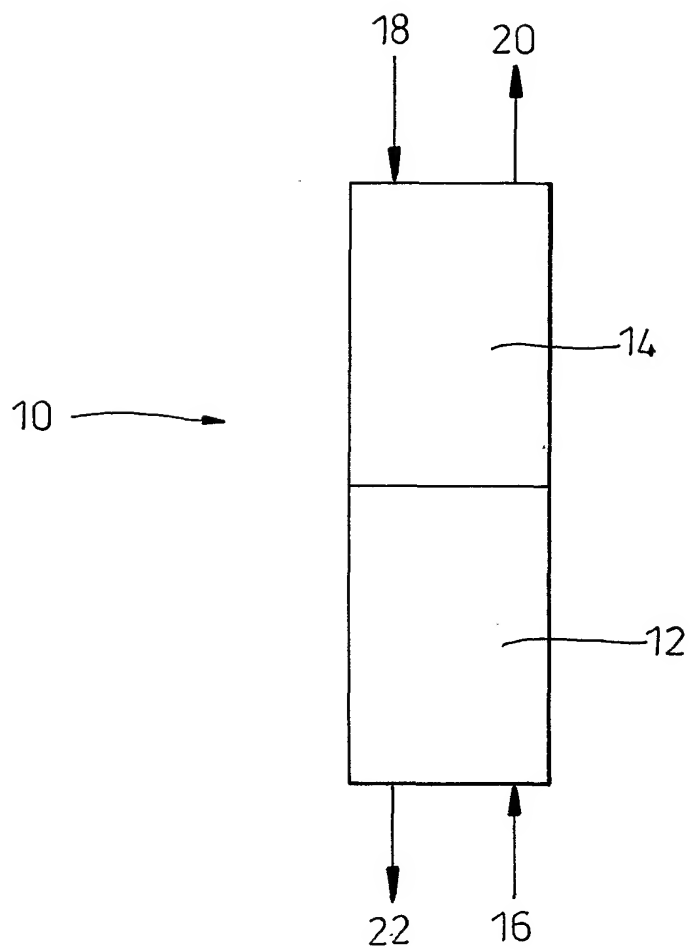
12. A process according to any one of claims 6 to 11, wherein stage (ii) is conducted at a temperature of from 100°C to 500°C and below the temperature of stage (i).

13. A process according to claim 9, wherein a moving bed moves the aluminium based material from the reaction zone for stage (ii) to the reaction zone for stage (i) in a direction counter-current to the gas flow.

14. A process according to any one of the preceding claims, wherein the gas residence time in each stage of the process is from 0.1 to 40 seconds.
15. A process according to any one of the preceding claims, further comprising stage (iii) in which at least one inorganic fluorine-containing compound is removed from the first gaseous mixture by deposition on a solid comprising an aluminium based material.
16. A process according to claim 15, wherein the solid used in stage (iii) comprises aluminium oxide, hydrated aluminium oxide, aluminium hydroxide, aluminium oxyfluoride or aluminium fluoride.
17. A process according to claim 15 or 16, wherein stage (iii) is conducted at a temperature of from 0 to 800°C and the reaction residence time is from 0.1 to 30 seconds.
18. A process according to any one of the preceding claims, wherein the solid used in stage (iii) is the same as the catalyst used in stage (i).
19. A process according to Claim 18, wherein stage (iii) is conducted at a temperature of from 0 to 500°C and a lower temperature than that at which stage (i) is conducted.
20. A process according to any one of claims 15 to 19, wherein the catalyst comprising an aluminium based material used in stage (i) is the same as the absorbent comprising an aluminium based material used in stage (ii) and the same as the solid comprising an aluminium based material used in stage (iii).

21. A process according to claim 20, wherein a moving bed moves the aluminium based material from the reaction zone for stage (ii) to the reaction zone for stage (i) and then to the reaction zone for stage (iii).
- 5 22. A process according to any one of the preceding claims wherein the aluminium based material or at least one of the aluminium based materials is activated or reactivated by treatment with steam.
- 10 23. A process according to any one of the preceding claims, wherein at least a proportion of the gas vented from stage (ii) is recycled to the reaction zone for stage (i) and/or stage (iii).

1/1

*Fig. 1*

INTERNATIONAL SEARCH REPORT

PCT/GB 02/00264

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 B01D53/68 B01D53/86

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	EP 0 885 648 A (HITACHI LTD) 23 December 1998 (1998-12-23) page 2, line 38 -page 3, line 15 page 3, line 42 -page 4, line 5 ---	1-5,10, 11,14,22 6-9,13, 15,16, 18,20, 21,23
X	EP 0 916 388 A (HITACHI LTD ;HITACHI ENG CO LTD (JP); HITACHI KYOWA ENGINEERING CO) 19 May 1999 (1999-05-19) page 5, line 14 - line 35 page 6, line 23 - line 59 page 7, line 34 - line 43 --- -/--	1-5,10, 12,22



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

15 May 2002

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

PCT/GB 02/00264

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	US 3 790 143 A (NIX T) 5 February 1974 (1974-02-05) column 2, line 49 -column 5, line 50 ----	6-9, 13, 15, 16, 18, 20, 21, 23
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PCT/GB 02/00264

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DERWENT-ACC-NO: 2002-627392

DERWENT-WEEK: 200830

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TITLE: Removal of fluorine-containing compound, e.g. hydrofluorocarbon or perfluorocarbon, from gaseous mixture involves contacting the mixture with an aluminum-based catalyst and removing hydrogen fluoride from the resulting gas mixture

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PATENT-ASSIGNEE: DRAPER L C[DRAPI] , INEOS FLOUR HOLDINGS LTD[INEON] , INEOS FLUOR HOLDINGS LTD[INEON] , SCOTT J D[SCOTT]

PRIORITY-DATA: 2001GB-001769 (January 24, 2001) ,
2001GB-001769 (January 24, 2002)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE
WO 02058824 A1	August 1, 2002	EN
EP 1353742 A1	October 22, 2003	EN
BR 200206518 A	February 17, 2004	PT
AU 2002226536 A1	August 6, 2002	EN
US 20040076569 A1	April 22, 2004	EN
JP 2004529868 W	September 30, 2004	JA
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DE 60201973 T2	March 2, 2006	DE
AU 2002226536 B2	April 13, 2006	EN

IN 200301016 P1 March 16, 2007 EN
 JP 4080336 B2 April 23, 2008 JA

DESIGNATED-STATES: AE AG AL AM AT AU AZ BA BB BG BR BY
 BZ CA CH CN CO CR CU CZ DE DK DM DZ
 EC EE ES FI GB GD GE GH GM HR HU ID
 IL IN IS JP KE KG KP KR KZ LC LK LR
 LS LT LU LV MA MD MG MK MN MW MX MZ
 NO NZ PH PL PT RO RU SD SE SG S I SK
 SL TJ TM TR TT TZ UA UG US UZ VN YU
 ZA ZW AT BE CH CY DE DK EA ES FI FR
 GB GH GM GR IE IT KE LS LU MC MW MZ
 NL OA PT SD SE SL SZ TR TZ UG ZM ZW
 AL AT BE CH CY DE DK ES FI FR GB GR
 IE IT LI LT LU LV MC MK NL PT RO SE
 SI TR AT BE CH CY DE DK ES FI FR G B
 GR IE IT LI LU MC NL PT SE TR

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
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IN 200301016P1	N/A	2002WO-GB00264	January 24, 2002
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IN 200301016P1	N/A	2003IN-DN01016	June 30, 2003
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US 6921519B2	Based on	2003US-466997	December 8, 2003

INT-CL-CURRENT :**TYPE****IPC DATE**

CIPP

B01D53/68 20060101

CIPP	B01D53/70	20060101
CIPP	C07B37/06	20060101
CIPS	B01D53/68	20060101
CIPS	B01D53/68	20060101
CIPS	B01D53/68	20060101
CIPS	B01D53/86	20060101
CIPS	B01D53/86	20060101
CIPS	B01D53/86	20060101
CIPS	B01J20/08	20060101
CIPS	B01J20/34	20060101
CIPS	C07B35/06	20060101
CIPS	C07B37/06	20060101

ABSTRACTED-PUB-NO: WO 02058824 A1

BASIC-ABSTRACT:

NOVELTY - Fluorine-containing compound(s) are decomposed and removed from a first gaseous mixture comprising the fluorine compound(s) and water vapor by contacting the first mixture with an aluminum-based catalyst to produce a second gaseous mixture of hydrogen fluoride and carbon oxides. The hydrogen fluoride is removed from the second mixture to produce a third gaseous mixture.

USE - Decomposing and removing fluorine-containing compounds, e.g. hydrofluorocarbon or perfluorocarbon, from aqueous gaseous mixture. The process may be used in the semiconductor industry where these gases are used for cleaning and etching.

ADVANTAGE - The process is simple, effective and industrially applicable. It provides a two stage hydrothermal treatment process having a high efficiency of decomposition of the fluorine containing compounds, where greater than 99% destruction efficiencies can be achieved. It also provides greater than 99% absorption

efficiency, thus eliminating the need for aqueous scrubbing post treatments.

EQUIVALENT-ABSTRACTS:

ORGANIC CHEMISTRY

Preferred Compound: The fluorine-containing compound is a hydrofluorocarbon or perfluorocarbon having 1-4C chain length (preferably tetrafluoromethane, trifluoromethane, perfluoropropane, octafluorobutane, pentafluoroethane, difluoromethane, tetrafluoroethane or perfluoroethane).

CHEMICAL ENGINEERING

Preferred Process: The first mixture is contacted with the aluminum-based material at 500-1000 degrees C. The hydrogen fluoride is removed from the second mixture by contacting it with an aluminum-based absorbent at a lower temperature of 100-500 degrees C. A moving bed moves the aluminum-based material from the first stage reaction zone (where the second mixture is produced) to the second stage reaction zone (where the hydrogen fluoride is removed from the second mixture) in a direction counter-current to the gas flow. The gas residence time in each reaction zone is 0.1-40 seconds. Inorganic fluoride-containing compound(s) are removed from the first mixture by deposition on an aluminum-based solid material at 0-800 degrees C (preferably 0-500 degrees C) for 0.1-3 seconds.

The moving bed is moved from the second reaction zone to the first reaction zone then to the third stage reaction zone (where the inorganic fluoride-containing compounds are removed from the first mixture). The same aluminum-based materials may be used in each reaction stage and can be activated or re-activated by steam treatment. A proportion of the gas vented from the first reaction zone is recycled to the other reaction zones.

INORGANIC CHEMISTRY

Preferred Material: The aluminum-based catalyst is aluminum oxide, hydrated aluminum oxide, aluminum hydroxide, aluminum oxyfluoride or aluminum fluoride. The aluminum-based absorbent is aluminum oxide, hydrated aluminum oxide, aluminum hydroxide or aluminum oxyfluoride. The aluminum-based material(s) comprises metal or metal compound of Groups 4-14 of periodic table.

Exhausted absorbent from a second stage reactor was placed into a first stage hydrolysis reactor. The second stage absorbent charge was replaced using fresh Engelhard Al-3996 alumina. The first stage reactor temperature was raised to 750 degrees C and the second stage absorber was heated to 250 degrees C while passing a water-saturated nitrogen stream (2500 ppm by volume) of tetrafluoromethane (CF₄). The H₂O:CF₄ feed ratio was about 20,000:2,500 by volume. The contact times were 2.1 second for the first stage and 4.2 seconds for the second stage. After 100 hours of operation, the CF₄ destruction efficiency was maintained at greater than 90% using the cascaded spent alumina absorbent. The hydrogen fluoride (HF) absorption efficiency was found to be 99.6% before exhaustion of the HF absorption capacity. The second stage charge of aluminum oxide was found to convert 70% to aluminum trifluoride.

TITLE-TERMS: REMOVE FLUORINE CONTAIN COMPOUND GAS
MIXTURE CONTACT ALUMINIUM BASED CATALYST
HYDROGEN FLUORIDE RESULT

DERWENT-CLASS: E16 J01

CPI-CODES: E10-H04A3; E11-Q02; E34-C02; E34-C03;
J01-E02D; N01-C02; N01-C03; N07-L01C;

CHEMICAL-CODES: Chemical Indexing M3 *01* Fragmentation
Code C009 C100 C101 C730 C800 C801 C804
C805 C806 C807 M411 M750 N163 N423 Q431
Q436 Q454 Specific Compounds R01712
Registry Numbers 219

Chemical Indexing M3 *02* Fragmentation
Code H6 H607 H685 H689 M280 M311 M321
M344 M363 M391 M416 M620 M750 N163 N423
Q431 Q436 Q454 Specific Compounds
R00378 Registry Numbers 155190

Chemical Indexing M3 *03* Fragmentation
Code H6 H685 M280 M311 M321 M343 M363
M391 M416 M620 M750 N163 N423 Q431 Q436
Q454 Specific Compounds R00367 Registry
Numbers 7606

Chemical Indexing M3 *04* Fragmentation
Code H6 H601 H607 H684 H685 H689 M280
M313 M321 M332 M344 M363 M391 M416 M620
M750 N163 N423 Q431 Q436 Q454 Specific
Compounds R08480 Registry Numbers 55953

Chemical Indexing M3 *05* Fragmentation
Code H6 H601 H608 H684 H685 M280 M312
M321 M332 M344 M363 M391 M416 M620 M750
N163 N423 Q431 Q436 Q454 Specific
Compounds R16771 Registry Numbers
133559

Chemical Indexing M3 *06* Fragmentation
Code H6 H601 H608 H684 M280 M311 M321
M342 M363 M391 M416 M620 M750 N163 N423
Q431 Q436 Q454 Specific Compounds
R07374 Registry Numbers 8406

Chemical Indexing M3 *07* Fragmentation
Code H6 H607 H685 H689 M280 M312 M321
M332 M344 M363 M391 M416 M620 M750 N163
N423 Q431 Q436 Q454 Specific Compounds

R08479 Registry Numbers 131442

Chemical Indexing M3 *08* Fragmentation
Code H6 H601 H609 H684 H689 M280 M312
M321 M332 M344 M363 M391 M416 M620 M750
N163 N423 Q431 Q436 Q454 Specific
Compounds R16770 Registry Numbers
108605

Chemical Indexing M3 *09* Fragmentation
Code H6 H601 H607 H608 H609 H681 H682
H683 H684 H685 H689 M210 M211 M212 M213
M214 M215 M216 M231 M232 M233 M250 M280
M281 M311 M312 M313 M314 M315 M320 M321
M331 M332 M333 M340 M342 M343 M344 M363
M391 M416 M620 M750 N163 N423 Q431 Q436
Q454 Markush Compounds 007329001

Chemical Indexing M3 *10* Fragmentation
Code A313 A940 C009 C100 C108 C550 C730
C801 C803 C804 C805 C807 M411 M730 M781
N163 N423 Q421 Q431 Q436 Q454 Q508
Specific Compounds RA8500 Registry
Numbers 593991

Chemical Indexing M3 *11* Fragmentation
Code A313 A940 C108 C550 C730 C801 C802
C803 C804 C805 C807 M411 M730 M781 N163
N423 Q421 Q431 Q436 Q454 Q508 Specific
Compounds R01544 Registry Numbers
130157 205530 92

Chemical Indexing M3 *12* Fragmentation
Code A313 A940 C101 C108 C550 C730 C801
C802 C804 C805 C807 M411 M730 M781 N163
N423 Q421 Q431 Q436 Q454 Q508 Specific
Compounds R02020 Registry Numbers
129331 87080

Chemical Indexing M3 *13* Fragmentation
Code A313 A940 C009 C100 C730 C801 C803

C804 C805 C806 C807 M411 M730 M781 N163
N423 Q421 Q431 Q436 Q454 Q508 Specific
Compounds R01796 Registry Numbers 2234

UNLINKED-DERWENT-REGISTRY- ; 0367U ; 0378U ;
NUMBERS: 1544U ; 1544S ; 1712U ;
1796U ; 1796S ; 2020U ;
2020S

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: 2002-176964